



Experimental study on the influence of dimethylamine on the detection of gas phase sulfuric acid using chemical ionization mass spectrometry (CIMS)

L. Rondo, M. Leiminger, M. Simon, S. Ehrhart, C. Williamson, A. Praplan, A. Kürten, J. Kirkby, J. Curtius, and CLOUD Collaboration

Citation: [AIP Conference Proceedings](#) **1527**, 374 (2013); doi: 10.1063/1.4803281

View online: <http://dx.doi.org/10.1063/1.4803281>

View Table of Contents: <http://scitation.aip.org/content/aip/proceeding/aipcp/1527?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Measurement of neutral sulfuric acid-dimethylamine clusters using CI-API-TOF-MS](#)

AIP Conf. Proc. **1527**, 377 (2013); 10.1063/1.4803282

[Laser resonance ionization mass spectrometry for failed fuel detection and location in the experimental fast reactor JOYO](#)

AIP Conf. Proc. **584**, 125 (2001); 10.1063/1.1405592

[Study of laser resonance ionization mass spectrometry using a glow discharge source](#)

AIP Conf. Proc. **329**, 316 (1995); 10.1063/1.47573

[Chemical precursor to optical damage detected by laser ionization mass spectrometry](#)

Appl. Phys. Lett. **52**, 2205 (1988); 10.1063/1.99766

[Gas Analysis by Photo-Ionization Mass Spectrometry](#)

J. Appl. Phys. **37**, 2812 (1966); 10.1063/1.1782129

Experimental study on the influence of dimethylamine on the detection of gas phase sulfuric acid using Chemical Ionization Mass Spectrometry (CIMS)

L. Rondo^a, M. Leiminger^a, M. Simon^a, S. Ehrhart^a, C. Williamson^a,
A. Praplan^{b,c}, A. Kürten^a, J. Kirkby^d, J. Curtius^a,
and the CLOUD collaboration

^a*Institute for Atmospheric and Environmental Sciences, Goethe University of Frankfurt, Germany*

^b*Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, Villigen, Switzerland*

^c*Department of Physics, University of Helsinki, University of Helsinki, Finland*

^d*CERN, Geneva, Switzerland*

Abstract. Based on quantum chemistry calculations it has been suggested that the quantitative detection of gas phase sulfuric acid (H_2SO_4) by use of Chemical Ionization Mass Spectrometry (CIMS) could be biased in the presence of gas phase amines such as dimethylamine (DMA). An experiment was set up at the CLOUD aerosol chamber to test the quantitative detection of H_2SO_4 by CIMS by directly comparing the measured H_2SO_4 with and without DMA being present in the sample air. It was found that the H_2SO_4 cluster distribution changes but the CIMS detection efficiency is not strongly influenced.

Keywords: Chamber study, CLOUD experiment, sulfuric acid, new particle formation.

PACS: 82.60.Nh

INTRODUCTION

The nucleation of particles in the atmosphere is an important source for the atmospheric particle population and model calculations suggest that it could be responsible for about half of the global cloud condensation nuclei¹. Sulfuric acid (H_2SO_4) is widely recognized as the most important substance driving atmospheric aerosol nucleation². The method commonly used to detect gas phase H_2SO_4 is Chemical Ionization Mass Spectrometry (CIMS) which allows very sensitive detection of H_2SO_4 down to levels below 1×10^5 molecule per cubic centimeter^{3,4}. For detection with a mass spectrometer, H_2SO_4 is converted into bisulfate ions (HSO_4^-) by reaction with nitrate ions (NO_3^-) which can be clustered with nitric acid (HNO_3) or water molecules. Viggiano et al. showed that these reactions proceed with reaction rates close to the collision limit⁵. Recently, Kurtén et al. raised the question in how far this detection scheme is still valid if amines are present in the sample air⁶. Potentially the reaction with NO_3^- could be considerably less efficient if the H_2SO_4 molecules are each clustered with one or two dimethylamine (DMA) molecules. As these clustered H_2SO_4 molecules will continue to participate in the nucleation and growth – most

likely even more efficiently than the bare molecules – it is desired to measure the gas phase concentration of H_2SO_4 molecules regardless of whether they occur as the bare H_2SO_4 molecule or clustered with amines (or other molecules such as water or ammonia). The detection of gas phase H_2SO_4 could be interpreted to yield much lower H_2SO_4 concentration if the detection scheme was less efficient in the presence of amines. Although this effect was predicted to be only on the order of ten percent by the most reliable quantum chemistry computations⁶ it was decided to investigate this potential influence by a dedicated experimental study at the CLOUD aerosol chamber at CERN.

EXPERIMENTAL METHODS

The CLOUD aerosol chamber⁷ allows the stable in situ production of gaseous H_2SO_4 from the $\text{SO}_2 + \text{OH}$ reaction⁸. The H_2SO_4 concentration is monitored by a well-calibrated CIMS instrument³ (THS Instruments) as well as CI-APiTOF mass spectrometry⁴ (Tofwerk AG/Aerodyne Research, Inc.). It is an important advantage of the CLOUD aerosol chamber that contamination by amines, or other condensable organic or inorganic species are kept to extremely low levels (few pptv level or below) and a large number of these species is constantly monitored. Furthermore, loss of H_2SO_4 due to nucleation, wall losses and gas dilution in the chamber is monitored as well by various instruments and other potentially influencing factors such as relative humidity, gas temperature and pressure are also kept precisely constant⁷. This allows conducting nucleation experiments and other process studies at atmospherically-relevant levels.

We performed a series of measurements by creating a range of different H_2SO_4 concentrations (H_2SO_4 ranging from 1×10^6 to $1 \times 10^8 \text{ cm}^{-3}$) in the CLOUD chamber, first without any measurable amounts of DMA present in the chamber ($< 0.2 \text{ pptv}$), and then repeating the exact same measurements while introducing DMA at levels of 10 and 40 pptv into the chamber. DMA levels are monitored by use of ion chromatography⁹.

RESULTS

While the additional DMA substantially influences the observed cluster distribution, the detailed analysis shows that the detection efficiency of the CIMS is not affected strongly by the presence of DMA. Results will be quantified and discussed at the conference.

ACKNOWLEDGMENTS

We would like to thank CERN for supporting CLOUD with important technical and financial resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC Seventh Framework Programme (Marie Curie Initial Training Network "CLOUD-ITN" no. 215072, MC-ITN "CLOUD-TRAIN", no. 316662, and ERC-Advanced "ATMNUCLE" grant no.

227463), the German Federal Ministry of Education and Research (project nos. 01LK0902A and 01LK1222A), the Swiss National Science Foundation (project nos. 200020_135307 and 206620_130527), the Academy of Finland Center of Excellence program (project no. 1118615), the Academy of Finland (CoE project no. 1118615, LASTU project no. 135054), the Nessling Foundation, the Austrian Science Fund (FWF; project no. P19546 and L593), the Portuguese Foundation for Science and Technology (project no. CERN/FP/116387/2010), the Swedish Research Council, Vetenskapsrådet (grant 2011-5120), the Presidium of the Russian Academy of Sciences and Russian Foundation for Basic Research (grants 08-02-91006-CERN and 12-02-91522-CERN), and the U.S. National Science Foundation (grants AGS1136479 and CHE1012293).

REFERENCES

1. J. Merikanto et al., *Atmos. Chem. Phys.* **9**, 8601-8616 (2009).
2. S.-L. Sihto et al., *Atmos. Chem. Phys.* **6**, 4079-4091 (2006).
3. A. Kürten et al., *J. Phys. Chem. A* **116**, 6375-6386 (2012).
4. T. Jokinen et al., *Atmos. Chem. Phys.* **12**, 4117-4125 (2012).
5. A. A. Viggiano et al., *J. Chem. Phys. A* **101**, 8275-8278 (1997).
6. T. Kurtén et al., *Atmos. Chem. Phys.* **11**, 3007-3019, (2011).
7. J. Kirkby et al., *Nature* **476**, 429-433 (2011).
8. A. Kupc et al., *J. Aerosol Sci.* **42**, 8, 535-543, (2011).
9. A. P. Praplan et al., *Atmos. Meas. Tech.* **5**, 2161-2167 (2012).